Surface and Interface Science Laboratory
Chief Scientist: Yousoo Kim (D.Eng.)

(0) Research field

CPR Subcommittee**:** Chemistry

Keywords:
Scanning tunneling microscopy, Surface and Interface, Energy transfer and conversion, Single-molecule chemistry and spectroscopy

(1) Long-term goal of laboratory and research background

Our research focuses on **describing the details of energy transport and conversion at solid surfaces and molecular interfaces in the nanoscale regime.** Excitation of molecules triggers various important energy conversion processes, such as luminescence, photochemical reactions, and photovoltaics. Detailed understanding of the molecular excited states is crucial to develop organic energy conversion devices based on opto-electronic/opto-chemical processes. We developed a scanning tunneling microscope (STM) combined with optical systems both for photon detection and for optical illumination to investigate energy transfer, conversion and dissipation processes of various quantum states, such as spin, phonon, and exciton, confined in molecular interfaces from a single isolated molecule to well-ordered molecular assembles.

(2) Current research activities (FY2019) and plan (until Mar. 2025)

[Research activities in FY2019]

① Discovery of a new mechanism for controlling exciton formation and establishment of theoretical analysis framework

We have found a way to significantly reduce the amount of energy required by the organic light-emitting diodes (OLEDs) [Nature 570 (2019) 17736] [Press Release] (Fig.1). The advance was achieved by developing a new way to manipulate the excitons that are key to the transport of electrons within OLEDs. These findings could become a general working principle for novel OLEDs with low operating voltage. We also established a theoretical framework to explain how the electroluminescence can work at a single molecule, based on the Coulomb interaction between charges in the excitonic state [Nano Lett. 19 (2019) 2803]. The developed theory provides a unified description of the electron transport and optical properties of a single molecule, and thereby, it contributes to a microscopic understanding of optoelectronic conversion in single molecules at nanometer-scale junctions.

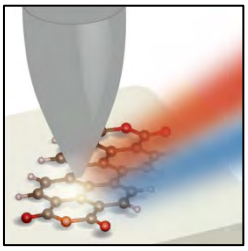

Fig.1. A schematic of single-molecule electroluminescence under an STM tip

② Utilizing a localized surface plasmon to controlling single-molecule chemical reactions and to developing local spectroscopic techniques

Optical illumination to the STM tip apex generates a localized surface plasmon (LSP) that has been attracting great attention mainly as a novel near-field light source to overcome the diffraction limit of the optical wavelength. We have applied the LSP towards exploring the photodissociation mechanism of a single oxygen molecule (Fig. 2) [Angew. Chem. Int. Ed. 59 (2020) 7960] [RIKEN Research Highlight]. This study revealed that why shining light on silver nanoparticles causes oxygen molecules to break off. We also utilized the LSP as a nanocavity to achieve single-molecule resonance tip-enhanced Raman spectroscopy (TERS) for detecting vibrations of a single molecule (Fig. 3) [Nat. Nanotechnol. 15 (2020) 105] [RIKEN Research Highlight], which allows us to produce different spatial maps of the molecule for different vibrational modes. The TERS technique was then applied to the chemical characterization of the self-assembled monolayer formed on an electrode surface in the electrochemical cell (Fig. 4) [J. Phys. Chem. C 123 (2019) 2953].

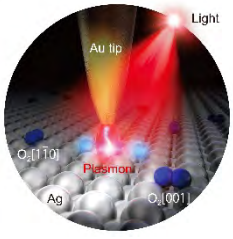

Fig.2. Dissociation of individual oxygen molecules by the LSP.

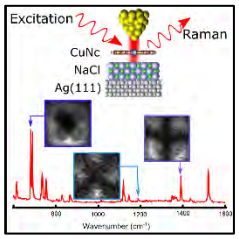

Fig.3. Vibrational mode mapping of a single molecule by TERS

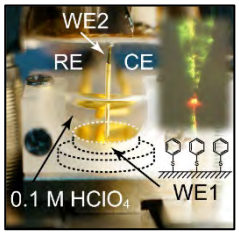

Fig.4. Experimental setup of electrochemical TERS

③ Molecular-scale investigation of self-assembled organic monolayers

Establishing a way to fabricate well-ordered molecular structures is a necessary step towards advancement in molecule-based devices. Especially, the fabrication of homogeneous organic monolayer requires precise control of intermolecular interactions and molecule-substrate interactions. We have observed how 'achiral' molecules (that is, molecules that are identical to their mirror image) can arrange themselves on a surface to form different chiral structures depending on how densely they cover the surface1. This finding could be useful for applications such as catalysis and sensors (Fig. 5) [Angew. Chem. Int. Ed. 58 (2019) 9611] [RIKEN Research Highlight]. By observing individual atoms as they rearrange themselves step by step to form a covalent bonding network, we also have cast new light on the route by which halogenated aromatic molecules join together on a silver surface (Fig.6) [Angew. Chem. Int. Ed. 58 (2019) 17736] [RIKEN Research Highlight]. These insights promise to help engineers generate atomically precise nanomaterials and electronic devices.

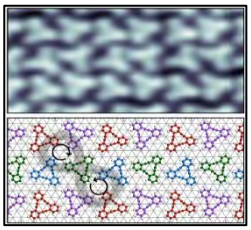

Fig.5. Chiral structure of an organic monolayer.

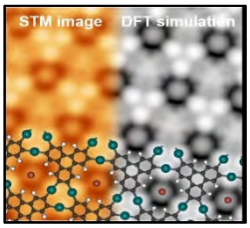

Fig.6. Covalent bonding network of an organic monolayer

④ Creation of a novel 2D material, graphenol (C_6OH_1)

We explored a chemical route to synthesize centimeter-scale stoichiometric "graphenol (C_6OH_1)", a 2D crystalline alcohol, via vapor phase hydroxylation of epitaxial graphene on Cu(111) (Fig. 7) [Nano Lett. 20 (2020) 2107]. Atomically-resolved STM images revealed this highly-ordered configuration of graphenol and low energy electron diffraction studies on a large-area single crystal graphene film demonstrated the feasibility of the same superstructure being achieved at the centimeter length scale.

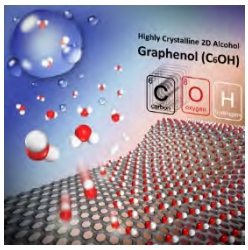

Fig.7. Fabrication of a graphenol

(3) Members

as of March, 2020

(Chief Scientist)
Yousoo Kim
(Senior Research Scientist)
Norihiko Hayazawa, Yasuyuki Yokota, Hiroshi Imada
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Emiko Kazuma
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(Contract Researcher)
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(Postdoctral Researcher)
Wong Raymond, Miyabi Imai
(Technical Staff)
Yoshiko Shimizu
(Junior Research Associate)
Lee Minhui
(International Program Associate)
Zoh Inhae
(Student Trainee)
Kosuke Kimura, Bae Jaehyun
(Assistant)
Chikako Kuramochi
(Part-time Worker)
Yuki Hasegawa

(4) Representative research achievements

1. "Selective triplet exciton formation in a single molecule", K. Kimura, K. Miwa, H. Imada, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, M. Galperin, and Y. Kim, **Nature** 570 (2019) 210-213.
2. "Atomic-scale visualization of the stepwise metal-mediated dehalogenative cycloaddition reaction pathways: competition between radicals and organometallic intermediates", C. Zhang, E. Kazuma, and Y. Kim, **Angew. Chem. Int. Ed.** 58 (2019) 17736-17744.
3. "Single-molecule resonance Raman effect in a plasmonic nanocavity", R.B. Jaculbia, H. Imada, K. Miwa, T. Iwasa, M. Takenaka, B. Yang, E. Kazuma, N. Hayazawa, T. Taketsugu, and Y. Kim, **Nat. Nanotechnol.** 15 (2020) 105-110.
4. "Single-molecule study of a plasmon-induced reaction for a strongly chemisorbed molecule", E. Kazuma, M. Lee, J. Jung, M.l Trenary, and Y. Kim, **Angew. Chem. Int. Ed.** 59 (2020) 7960-7966.
5. "Centimeter-scale and highly crystalline 2D alcohol: evidence for graphenol (C_6OH)", H. Lim, Y. Park, M. Lee, J.-G. Ahn, B.-W. Li, D. Luo, J. Jung, R. Ruoff, and Y. Kim, **Nano Lett.** 20 (2020) 2107-2112.

Supplementary

Group Photo

Laboratory Homepage

http://www.riken.jp/en/research/labs/chief/surf_interf/

http://www2.riken.jp/Kimlab/